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OCTAVIUS: Evaluation of flexibility and operability of amine based post combustion CO_2 capture at the Brindisi Pilot Plant

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Abstract

Solvent storage is an option for amine based post combustion capture that can be used to de-couple the capture of CO_2 and the energy demand of the process. In this process, electricity output of a power station is temporarily increased by diverting steam from the CO_2 capture plant back to the steam turbines. To maintain CO_2 capture, an increased solvent inventory is deployed to provide fresh solvent for capture and storage tanks are used to store solvent to be regenerated at a later time. The OCTAVIUS project aimed to evaluate the performance of this solvent storage process through testing at the Brindisi CO_2 capture pilot facility. This facility is owned and operated by the Italian utility ENEL and is based at ENEL's Federico II coal power plant in southern Italy, which provides coal-fired flue gas to the pilot plant.

Over one week the solvent storage process was successfully demonstrated at large scale; four tests were completed to assess different operating modes and conditions. For all tests it was found that it took significant amount of time for the stripper to stabilize. This stabilization time meant that in one pass, the solvent could not be fully regenerated. This also resulted in the regeneration being at non-optimal conditions greatly increasing amount of energy required for regeneration. Follow up work should seek to ensure the plant design is appropriate for solvent storage to avoid the issues faced in this experiment. OCTAVIUS will investigate solvent storage in a flexible market model in 2015.

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: Post Combustion Capture ; CCS; solvent storage; intermittant stripping; pilot plant; MEA; CO2 capture;flexibility

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1. Introduction

The path towards reducing CO_2 emissions to prevent climate change has led to some of the most significant challenges and requirements for the electricity industry. Typically consisting of large point sources of energy production, power generation is seen as potentially cheaper to decarbonise than geographically diverse sources such as agriculture and transportation. As an energy source for many other industry and residential areas it is expected the electricity system will fully be decarbonised providing a source of low CO_2 energy for all sectors. This has principally been supported by the rapid growth of renewable technologies, in particular wind and solar energy. This has been driven by combination of targets for CO_2 reduction and renewables, and also significant subsidies.

Wind & solar renewable technologies have a significant disadvantage; they are intermittent and cannot be deployed on demand. Therefore when the renewable energy is not available, on demand energy sources, typically fossil plants, must increase their output. It should be noted this also works the opposite way, when too much power is produced generation sources must be quickly shutdown to protect the electricity grid, this could be renewable generation or conventional depending on the grid situation, however both increase the overall cost of energy. The variation in output from renewable technologies can be relatively rapid and large as a percentage of their capacity. At low market penetration, existing grids and procedures can generally cope with these changes. However as these intermittent renewable energy sources become a larger percentage of the electricity generation, the requirement for on-demand flexible plant will increase.

If, as above, electricity supply must be completed decarbonised, fossil fuel plants must be fitted with Carbon Capture and Storage (CCS) technologies to remove and sequester CO_2. However it is likely these technologies will operate in a future electricity market with high penetration of renewable energy, therefore they may also be required to operate flexibly depending on the market conditions. There are several challenges to ensuring CO_2 capture plants and the transportation and storage chain can achieve the required flexibility, such as start-up & shutdown times, ramp rates and full-chain stability. In this work we present the investigation of solvent storage as a method of increasing the flexibility of post combustion CO_2 capture technologies while maintaining CO_2 capture at all times. [1]

Solvent storage is an option for amine based post combustion capture that can be used to de-couple the capture of CO_2 and the energy demand of the process. In this process electricity output of a power station is temporarily increased by diverting steam from the CO_2 capture plant back to the steam turbines. To maintain CO_2 capture, an increased solvent inventory is deployed to provide fresh solvent for capture and storage tanks are used to store solvent to be regenerated at a later time [2, 3]. This process is described in detail in section 2.

The OCTAVIUS project aimed to evaluate the performance of this solvent storage process through a large scale demonstration at the Brindisi CO_2 capture pilot facility. This facility is owned and operated by the Italian utility ENEL and is based at ENEL's Federico II coal power plant in southern Italy, which provides coal-fired flue gas to the pilot plant. This is described in more detail in section 3.

Section 4 and 5 describe the tests undertaken and the results, section 6 summarises the conclusions of this work.

Nomenclature

CCS	Carbon Capture and Storage
DeNOx	Nitrogen Oxide(s) Removal
DeSOx	Sulphur Oxides(s) Removal
ESP	Electrostatic Precipitator
FF	Fabric Filter
FGD	Flue Gas Desulphurisation
MEA	Monoethanolamine
PFD	Process Flow diagram
SRD	Specific Reboiler Duty
WESP	Wet Electrostatic Precipitator

2. Post combustion Capture and Solvent Storage

Post combustion capture using amine solvents is one of the principle technologies to capture CO_2 from fossil power stations. Amines react reversibly with CO_2 and can therefore be used in a thermal swing separation process. In the typical design and amine based solvent is contacted with flue gas in an absorber column; the amine reacts and binds CO_2 into the liquid solvent, separating it from the flue gases. The resulting solvent, rich with CO_2, is then heated and contacted with steam in a stripper column. This reverses the reaction of amine and CO_2, and the liberated CO_2 is produced at high purity ready for pressurisation and transportation to a geological storage site. A generic post combustion capture process design is illustrated in Figure 1.

The energy required to operate this process is substantial. The largest single energy requirement is the heat energy required to strip CO_2 from the solvent and that accounts for around 50% of the demand, the remaining 50% is electricity primarily for CO_2 compression, but pumping of solvent and cooling water are also significant. Overall this has a large impact on the power output of the fossil power plants, for example, typical designs reduce the power output from coal power plants by 20-30% [4]

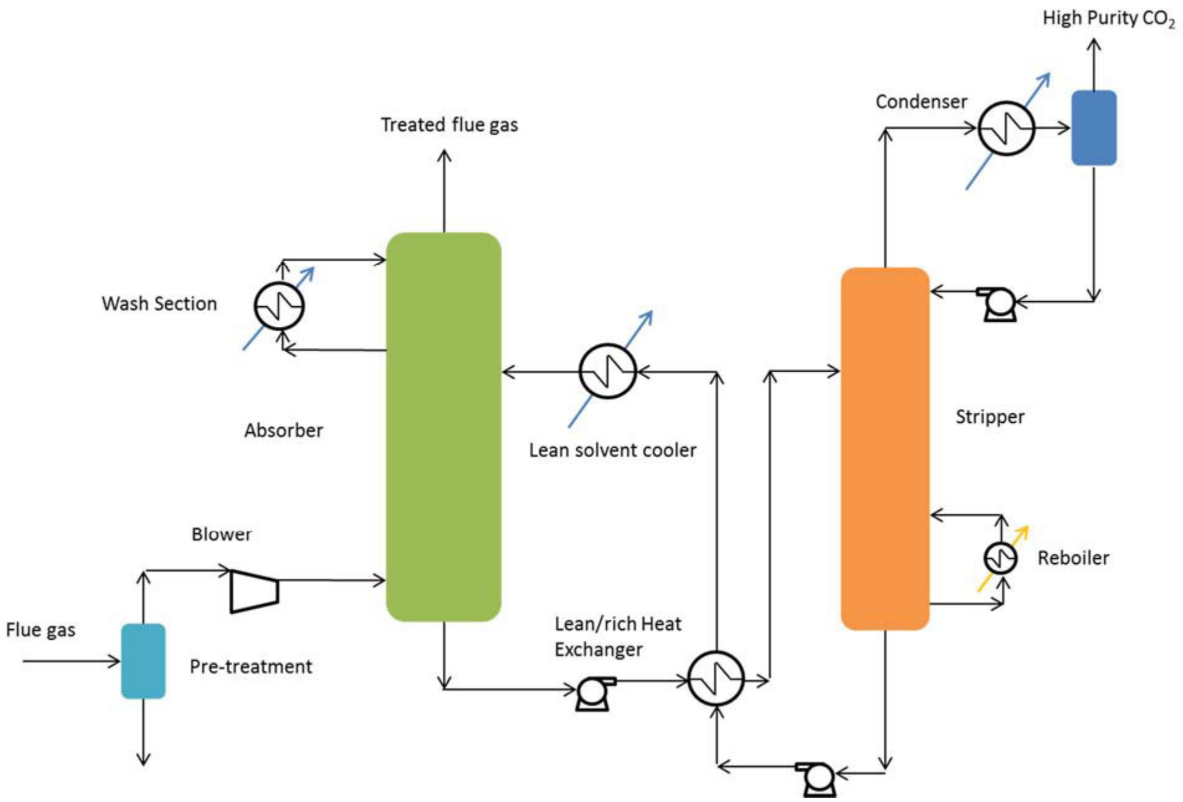

Figure 1 - Generic process flow diagram of an amine scrubbing process

In principle, if the regeneration of solvent is quickly halted it would result in a rapid increase in power output. However, in a typically designed CO_2 capture system, this would result in CO_2 capture rate decreasing; as the solvent is no longer being regenerated it would quickly become saturated with CO_2 and no longer able to react with the incoming flue gases to capture CO_2.

While solvent storage is a potential way to increase the flexibility of fossil plant, it could be impractical, some key reasons are:

- Regulations; these may not allow for operation without CO_2 capture, even for short periods.
- Cost; in several countries (notably those under the European Emissions Trading Scheme) CO_2 emissions credits must be bought.
- Technical limitations; shutting down the CO_2 capture plant would also involve shutting down CO_2 to compression, transportation and storage chain, which may technically be limited in their ability to do so.

Solvent storage is a technology that attempts to address the first two issues above by ensuring CO_2 is always captured. This process adds two large solvent tanks to the typical process design. One of these tanks holds a large quantity of lean solvent, when regeneration is turned down or off, this buffer of lean solvent is used to maintain CO_2

capture while the resulting rich CO_2 liquid is stored in the second tank. Figure 2 shows the generic PFD with these tanks.

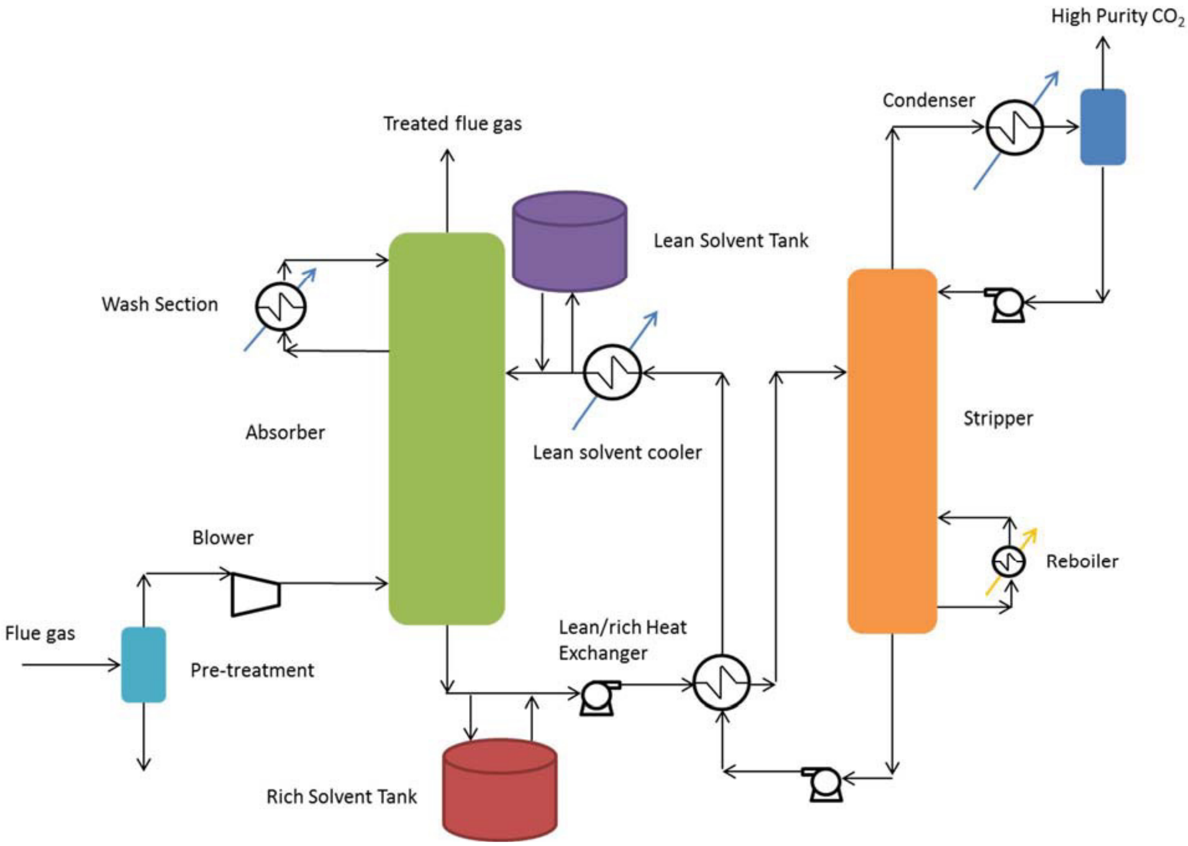

Figure 2 - Process flow diagram showing solvent tank locations

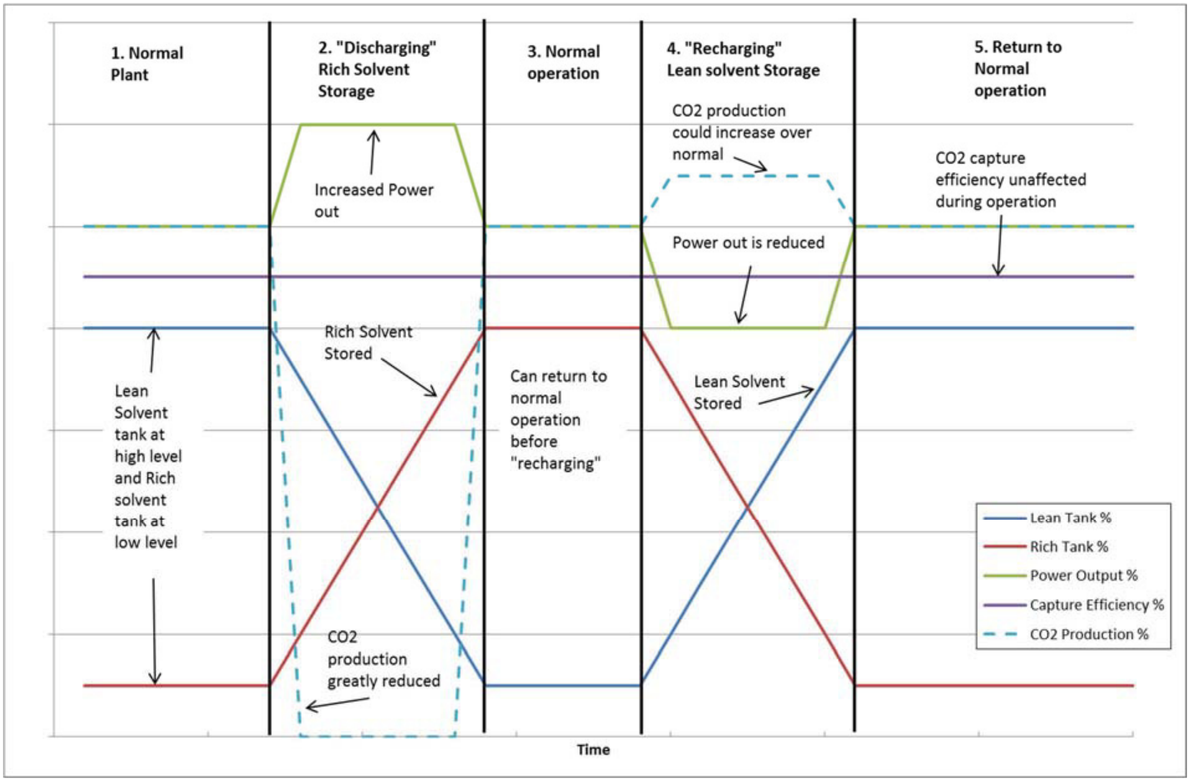

Figure 3 - Theoretical Solvent Storage Operation

The process can be considered similar to an energy storage device, where it is discharged and recharged as required. The following steps explain how this process would occur in a theoretical solvent storage operation and Figure 3 illustrates this process.

1. The plant is operating as normal; 90% capture efficiency, nominal power output. The lean tank has high level and rich tank has a low liquid level.

2. In “discharging” mode, steam to the stripper is diverted back to steam turbines and more power is produced. Lean solvent is supplemented from the lean solvent tank to maintain capture efficiency. Rich solvent is stored in rich solvent tank. CO_2 production is greatly reduced or ceases during this period.

3. The plant returns to nominal operation with typical power outputs and can continue this way indefinitely.

4. In “recharging” mode the stored rich solvent is regenerated and resulting lean solvent is returned to the lean solvent tank. During this period there are several options:

- Maintain power plant load and capture efficiency, but produce more CO_2
- Reduce capture rate to maintain CO_2 production and power plant load.
- Reduce power plant load to maintain capture rate and CO_2 production

5. Once the lean solvent tank is re-filled the system can return to normal operation ready to complete another “discharging” run as required.

For real applications there are many questions on what can practically be achieved, some of the key questions are:

In discharging mode:

- What are the full chain limitations? Can the compression, transportation and storage site cope with regular interruptions in CO_2 production?
- How low can CO_2 production be allowed to go, and if zero flow is acceptable, for how long? Is line packing required? How much does this cost?
- How quickly can steam flow be safely turned off to the reboiler?
- How much and how quickly will/can power increase (e.g. turbine limitations?)

In recharging mode:

- What is the maximum CO_2 flow capacity of the stripper/compression/transportation/storage?
- How quickly does the stripper return to optimum performance?
- What is the energy performance of regeneration during maximum stripping?
- What value is there in over-stripping the solvent? Is there an optimum lean loading?

Determining the answers to these technical questions is required to answer the overarching economic questions. Is solvent storage a cost effective means of increasing fossil plant flexibility, or what market conditions are required to make it cost effective?

In this work the aim is answer these questions for the capture plant side only, e.g. how does the performance of the capture plant vary during a solvent storage operations.

3. ENEL Pilot Plant Description

The CO_2 capture plant is located at the Brindisi sud (Federico II) power plant, which is a coal power plant consisting of 4 units with a capacity of 660 MWe each (total capacity 2640 MWe). Every unit is equipped with a DeNOx reactor, particulate collector (ESP or FF) and DeSOx reactor. The pilot plant is fed with the flue gas taken from unit number 4. The pilot plant is designed for a nominal gas flow rate of 10,000 Nm^3/h and can capture up to 2.5 tonnes of CO_2 per hour. Before CO_2 is captured the flue gas is pre-treated to further reduce SO_2 levels and two parallel WESP are installed to investigate the impact of particulates on CO_2 capture.

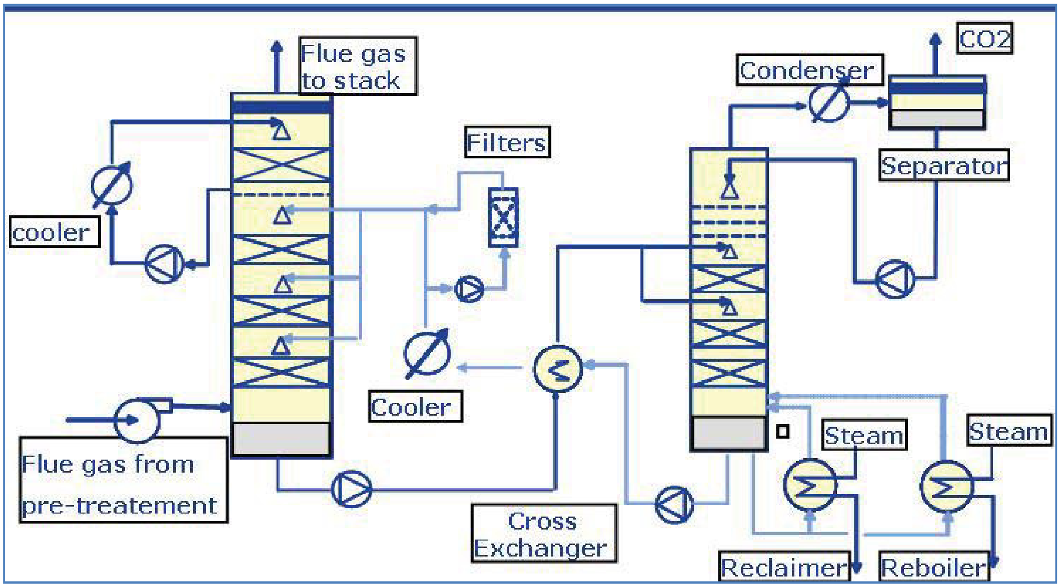

Figure 4 - Process flow diagram of the Brindisi Pilot Plant

Table 1 shows the nominal performance indicators of the pilot plant, when operating with a solvent of 30wt% Monoethanolamine (MEA).

Table 1 Brindisi Pilot plant - Key Performance Indicators

Process Parameter	Nominal Value
Solvent flow rate	30 m3/h
Amine	MEA
Solvent Amine Concentration	30wt%
Kg Steam/kg CO2	1.55
Specific Reboiler Duty	3395 KJ/kg
Flue Gas Flow rate	10000 Nm^3/h
CO_2 inlet concentration	11-12% Dry
Steam Flow	2800-2900 kg/h
CO2 production	2000 kg/h

This pilot facility is unusual because it has two large solvent storage tanks. In normal operation one of these tanks is used to store spare solvent, while the other is part of the normal solvent loop and acts as a solvent sump.

Since there are two tanks and they are large compared to the typical solvent flow rate, it was determined they could be used to for solvent storage, as we could separate rich solvent from lean solvent. However these tanks were not designed for this purpose, therefore they are not in the correct location.

Figure 5 below shows the setup of the tanks at the pilot facility.

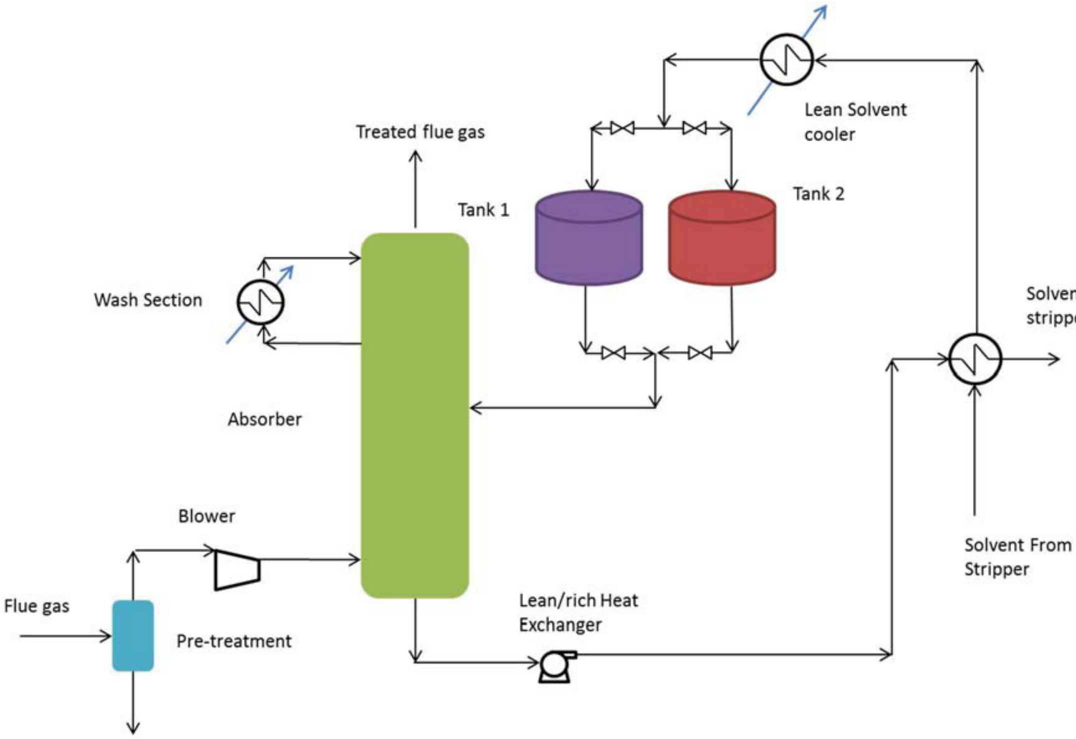

Figure 5 - Location of solvent storage tanks at Brindisi Pilot plant

The location of these tanks meant the only way to store rich solvent, was to pass it through the stripper. Equally rich solvent could not be directly sent to the stripper for regeneration, but had to pass through the absorber first.

To avoid the stripper or absorber impacting the results, it was agreed that during rich solvent storage the steam flow to the stripper would be completely turned off. When the reverse operation is operated and rich solvent regenerated, the flue gas to the absorber was also turned to off to prevent additional CO_2 enrichment of the solvent.

Additionally switching between the tanks could not be completed online because the control system was designed to trip in the eventuality of interruptions to the solvent flow rate. This meant when changing the operating regime the plant had to be temporarily shut down, tanks switched and the restarted. This took process generally took less than 30 minutes, but in a system designed for storage, this could be completely automated and thus made more efficient.

4. Test Plan

The pilot plant campaign at Brindisi operated over six weeks; of which one week was dedicated to testing solvent storage. Four tests were completed over this week.

1: Basic Solvent Storage cycle
The aim of this test was to investigate the most basic concept of this storage cycle.
In this steam to the stripper was switched off and lean solvent from Tank 1 was used to maintain 90% capture. Rich solvent was then stored in Tank 2 for regeneration later. When the lean solvent tank approached it minimum level the plant was shut down. The tanks were switch so the stored rich solvent could be directed to the stripper; the

stripper was then operated at its optimum operating mode until all the solvent had been once through the stripper. During this period the flue gas flow was set to zero to avoid interference with the rich solvent.

2: Maximum speed stripping
In this test the aim was to regenerate the solvent as fast as possible. As with the basic cycle, rich solvent was generated and stored in Tank 2. When regenerating the solvent, the stripper was operated at the highest possible solvent flow rate, which a correspondingly high steam flow rate.

3: Stripping from cold start
This test was aimed to investigate the impact of a cold stripper for regenerating solvent, to mimic the effect of a night time shutdown. Before the end of day two rich solvent was generated and stored. The plant was then shut down over night to cool. The plant was restarted in the morning and solvent was immediately regenerated in the stripper, using the normal operating parameters for solvent flow rate and steam flow.

4: Super lean solvent production and capture performances.
The aim of this final test was to investigate the benefit of over stripping the solvent. The rich solvent was again generated and stored in the same way as the basic cycle. When this was regenerated in the stripper, in this test the solvent flow was reduced and the steam flow maximized to strip the solvent as much as possible.

5. Results & Analysis

5.1. Basic Cycle Results:

The following figures show the main process parameter results from the first test. Figure 6 shows the steam flow was turned off at 08:15 and stored lean solvent was used to maintain CO_2 capture, although slightly lower than 90%. The resulting rich solvent was stored in the second tank as shown in Figure 8, this discharging period lasted 2 hour and 5 minutes. At 10:28 the plant was shut down temporarily to switch the tanks. The plant was restarted with just the stripper in operation. It took ~50 minutes to re-pressurize the stripper after which the CO_2 production peaked at ~1500 kg/h. The solvent was fully processed through the stripper after 2 hours and 36 minutes including pressurization time.

The lower capture rate is due to the slightly lower solvent flow rate that was kept constant during this part of the test (normally it is controlled to respond to varying CO_2 inlet concentration). The CO_2 production during recharging is significantly lower than normal; calculating the amount of CO_2 captured and released over the operations shows that during discharging approximately 4138 kg of CO_2 was captured however only 3168 kg was released when the solvent was regenerated in the stripper. This means during this period the solvent must not have been fully regenerated in one pass through the stripper, this is supported by the CO_2 loading figures in Figure 7, which shows during regeneration loading from the outlet of the stripper only reached 0.18 mol CO_2/mol MEA near the end of the "recharging" period. This is further supported by the specific steam demand and reboiler duty. It averaged 2.2 kg steam/kg CO_2 and 4810 kJ/kg, significantly higher than the normal performance, showing the system was operating in a non-optimally.

This reduced regeneration is likely due to time required for the stripper to reach the optimum, operation pressure and temperature. After restarting the steam flow to the reboiler, it took 50 minutes in this case to pressurise the column, and 93 minutes for the reboiler temperature to reach 118 ^{o}C. Additionally, due to the need to pass rich solvent through the stripper to the solvent tank, this meant that on restart, the stripper was full with rich solvent, instead of lean solvent as per normal operation.

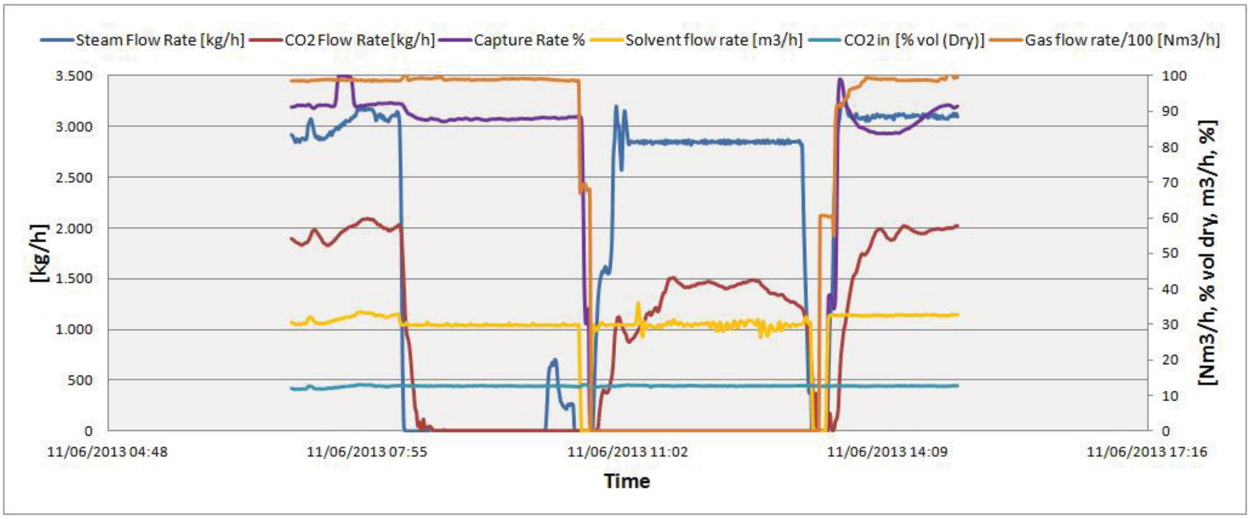

Figure 6 Intermittent stripping test: main process parameters normal cycle

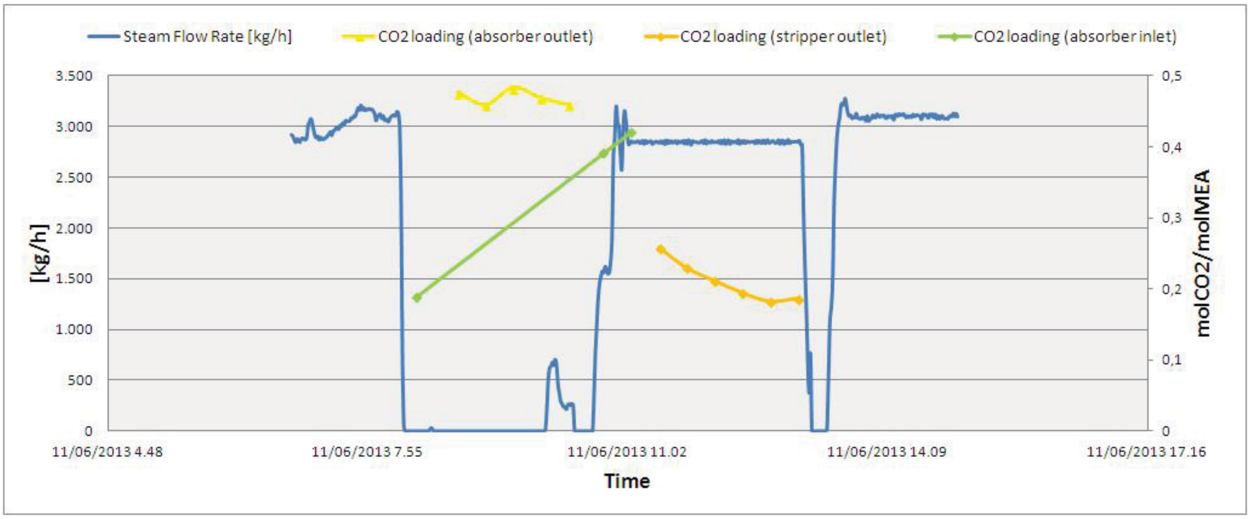

Figure 7: Intermittent stripping test: CO_2 loading vs. steam flow rate

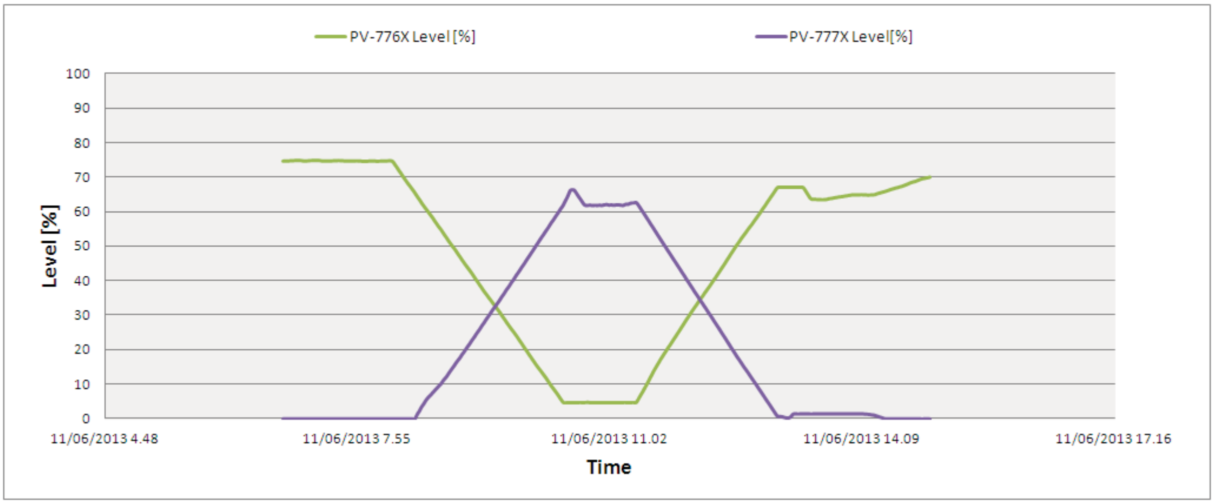

Figure 8 - Intermittent stripping test: % Level of PV-776X and PV-777X

5.2. Maximum Stripping Speed Test

During discharging phase, the steam flow was turned off as above to generate rich solvent. The solvent flow rate was fixed during this period, when the CO_2 concentration in the flue gas slightly decreased; this meant a capture rate at over 90%. The discharging phase lasted 2 hours 18 minutes and approximately 4132 kg CO_2 were captured.

During recharging the average solvent flow was 43 m^3/h, 43% more than the nominal flow rate. Steam flow was 52.5% more than standard at 4270 kg/h. As can be seen in Figure 9, the regeneration time is much shorter than the basic cycle at only 1 hour 40 minutes. The pressurization time is also significantly reduced at only 22 minutes. It should be noted however, that this fast stripping means the CO_2 flow rate is much higher than the nominal rate, at 2500 kg/h.

Similar to the basic case, significantly less CO_2 is released in the discharging phase compared to the recharging phase. This was due to the stabilization time for the stripper, meaning that the solvent took some time to reach steady lean loading. While the stabilization was faster than the normal case, due to the high flow rate a large percentage of the solvent had already been through the stripper. Figure 10 shows that the loading of the solvent entering the absorber immediately after regeneration is 0.27, which is significantly higher than the nominal lean loading of 0.18.

In this test, after the solvent was regenerated, rather than returning to normal operation immediately the plant was switched to a discharging mode again to generate rich solvent for the cold stripper case. It can be seen in Figure 9 that the capture rate was significantly reduced – supporting the lower loading, however the capture rate recovers after a short time back to 90%. Since at this point no solvent is being regenerated, this leaner solvent must be within the tank. This implies that solvent was not well mixed inside the tank; otherwise this behavior could not occur.

The specific steam demand and specific reboiler duty, were slightly improved for this case compared to the normal case at 1.98 kg Steam/kg CO_2 and 4332 kJ/kg CO_2 respectively. However the biggest benefit is the speed increase which could be essential to the economics of this system.

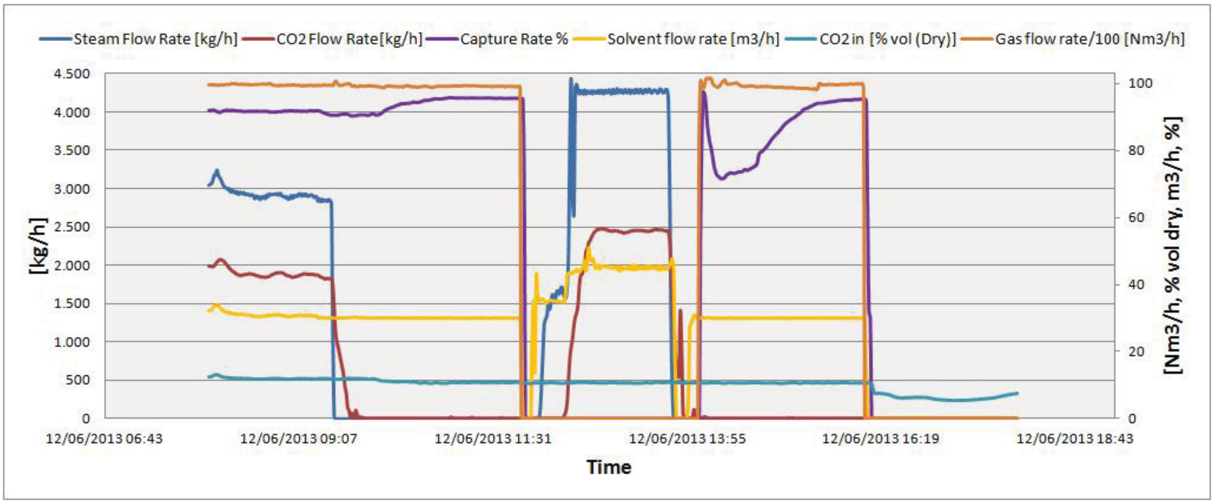

Figure 9 Main Process Parameters - Max Stripping Test

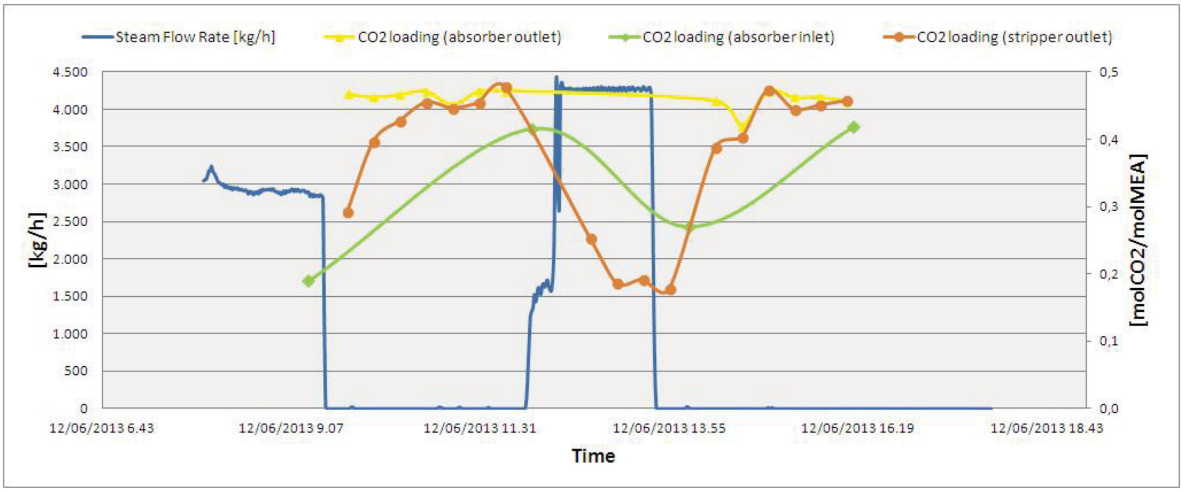

Figure 10 - CO_2 loading and steam flow - Max Stripping Test

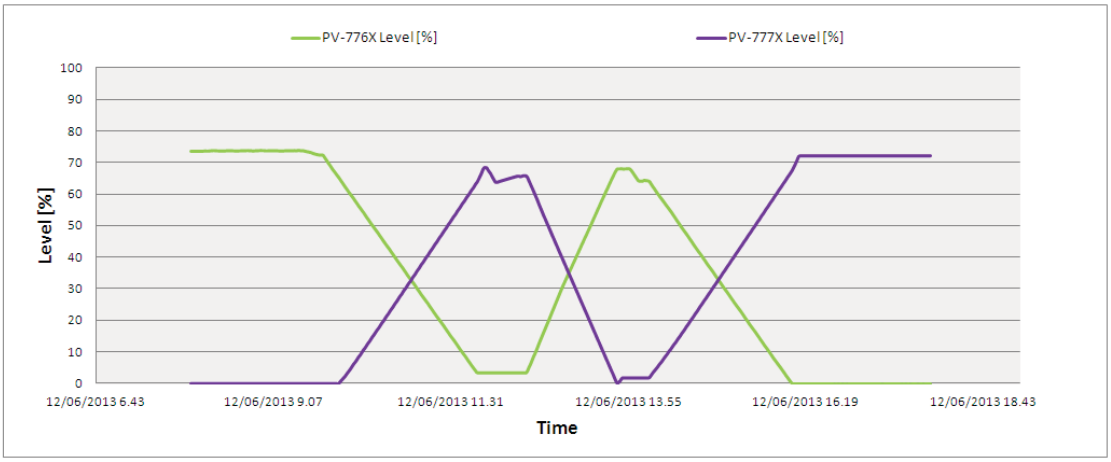

Figure 11 - Tank levels Max Stripping Test.

5.3. Stripping from cold start

After the maximum stripping test a discharging mode was immediately started to maximize the time the plant could be offline and cool down. The discharging mode in this case lasted 2 hour 14 minutes, however the capture rate averaged 78%.

The capture plant was shut down for over 16 hours and the stripper bottom temperature reduced to 42 ^{o}C. In this case the stripper was operated with nominal conditions. The regeneration period lasted 2 hour 49 minutes, pressurization time was 54 minutes therefore comparable to the basic cycle. CO_2 production flow was also very similar to the basic case at averaging at approximately 1500 kg/h.

It took 124 minutes for the reboiler to reach a temperature of 118 ^{o}C, therefore 34 minutes longer than the basic cycle.

As before less CO_2 was recovered than captured, supported by the lower lean loading figures. This led to lower CO_2 capture after returning to normal operation. There was a trip of the plant and this is the cause of the shutdown at around 13:00.

The slightly slower start up appeared to have, overall a fairly minor impact on the performance during start up.

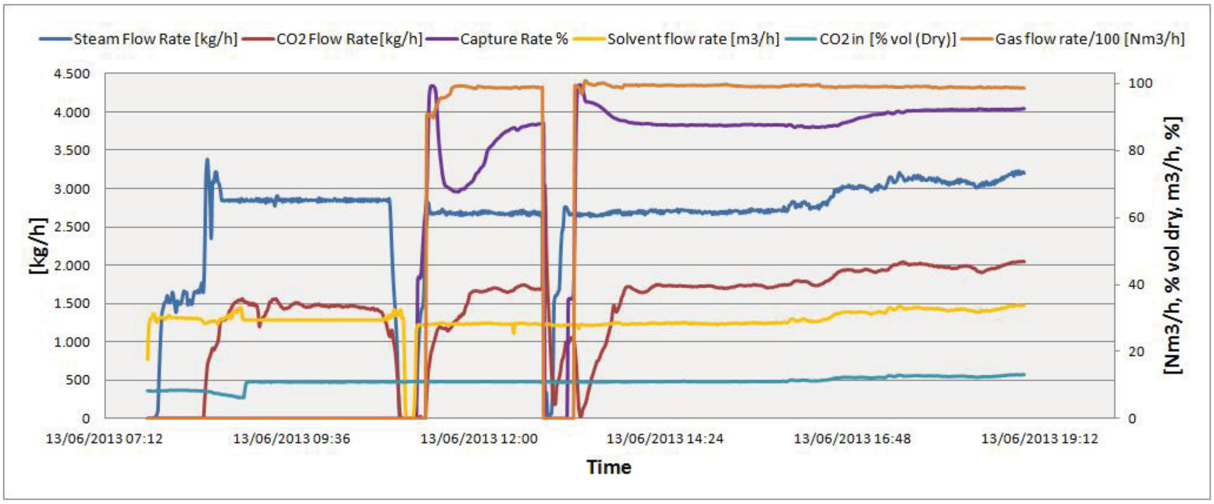

Figure 12 - Main Process Parameter - Cold Stripper Test

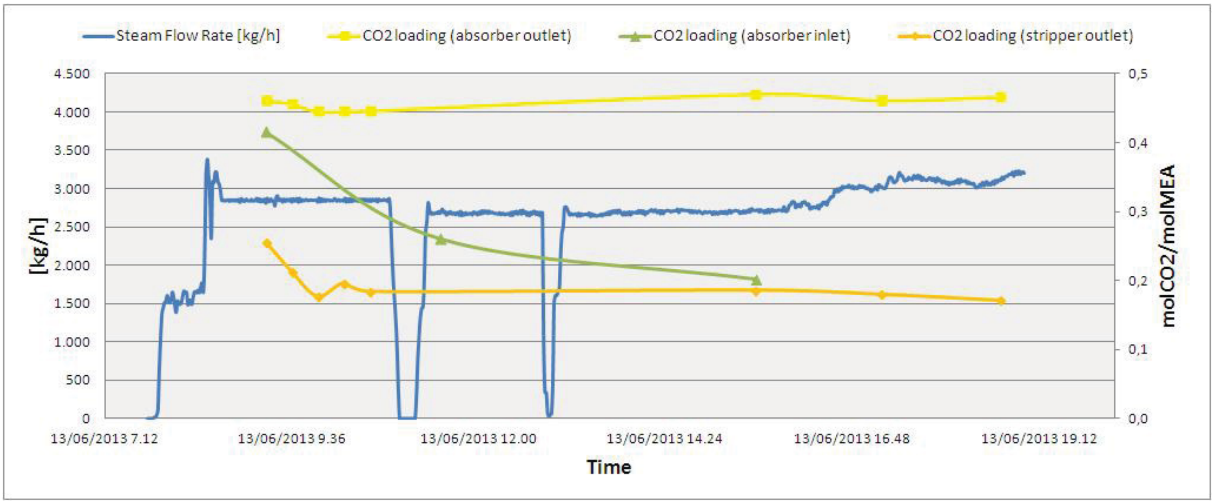

Figure 13 - Steam Flow and CO_2 Loading - Cold Stripper Test

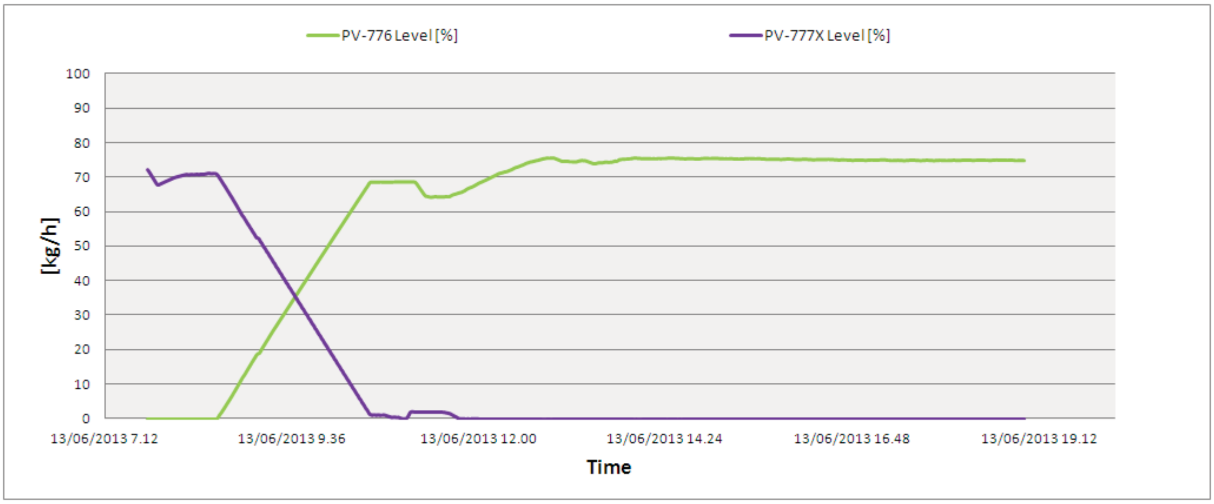

Figure 14 - Tank Levels - Cold Stripper test

5.4. Super lean solvent production test

As per the other cases the discharging state generated rich solvent over 2 hours and 15 minutes. In this case the capture rate was held steady at 90% for the majority of the period.

The solvent flow rate was set to be low in this case to allow a high ratio of solvent to steam to the reboiler. This means the regeneration was much slower than the previous cases, taking 4 hours and 38 minutes. There were some challenges maintaining constant flow conditions due to flashing in the cross heat exchanger. This caused the fluctuations in solvent flow rate, steam flow rate and CO_2 production. The CO_2 production varied significantly between minimum of 1000 kg/h to maximum of 2000 kg/h.

The time to pressurization was 45 minutes, similar to other cases; again less CO_2 was released during recharging as was captured during discharging, although it was slightly higher than the other cases. Again it took some time to reach the a low CO_2 loading in the solvent, however for this case the solvent was much leaner at 0.12 mol CO_2/mol MEA (nominal lean loading is ~0.18). Towards the end of the phase the steam flow was decreased to reduce the oscillations and regain plant control. This increased the loading slightly near the end of the campaign.

When returning to normal operation again at the nominal conditions the capture rate is reduced. However for this case it is shorter, only taking 44 minutes to reach 90% capture. However due to the extra lean solvent, the capture rate rises up to 96% capture and remains higher than 90% capture for several hours.

The significantly longer time for regeneration and difficulty with control means this is unlikely to be ideal case.

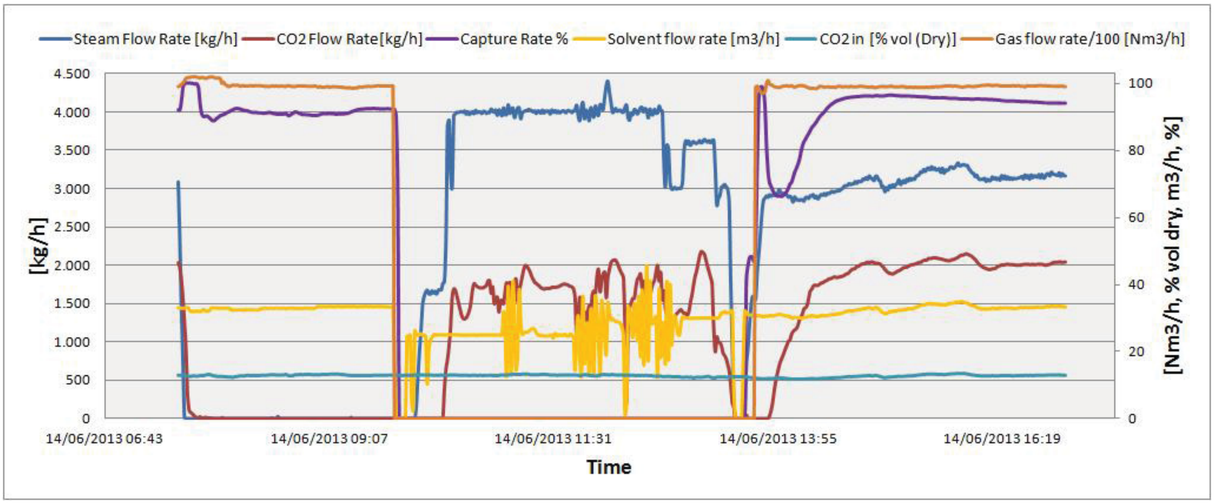

Figure 15 - Main Process Parameter - Super Lean Solvent Test

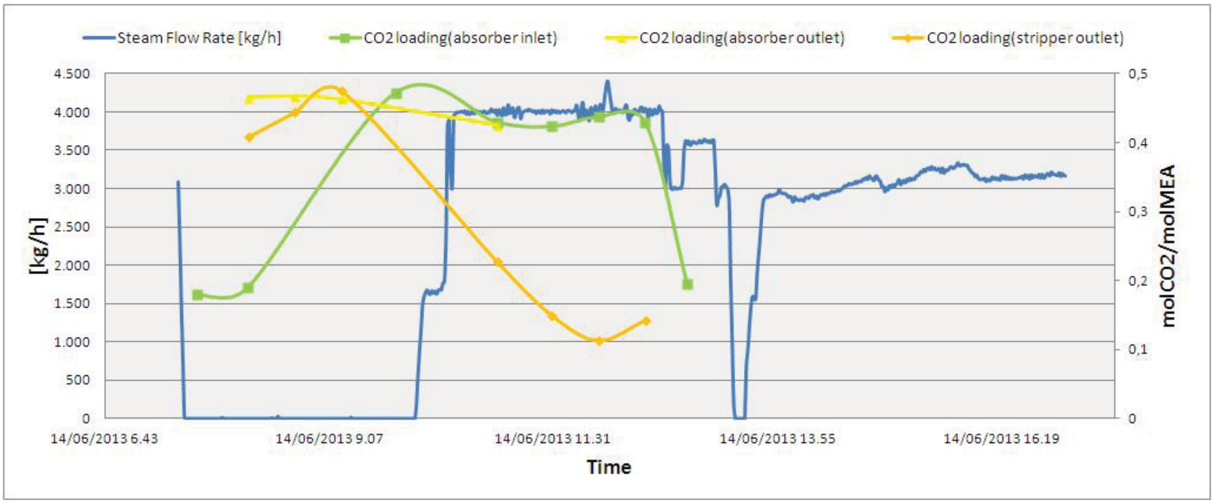

Figure 16 - Steam Flow and CO_2 loading - Super Lean Solvent test

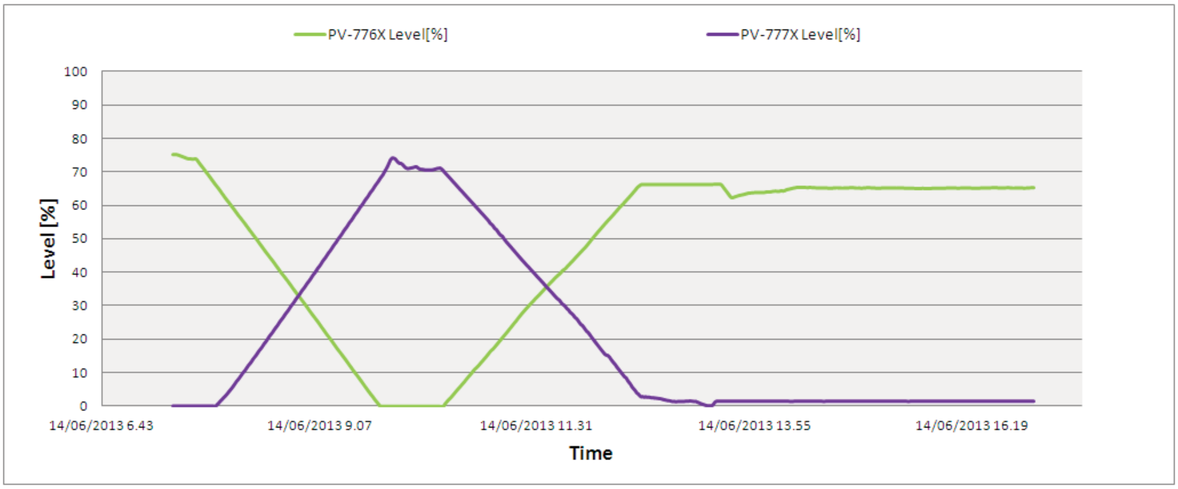

Figure 17 - Tank Level - Super Lean Solvent test

5.5. Summary

The table below (Table 2) shows a summary of all the key results for each of the test cases.

Table 2 - Summary of Key Results

		Basic Cycle	Maximum Speed stripping	Stripping from cold start	Super lean solvent production
Time Discharging	Hours : Mins	02:05	02:18	02:14	02:15
Time Recharging	Hours : Mins	02:36	01:40	02:49	04:38
Steam Saved Discharging	kg	6333	6105	5704	6969
Steam Required to Recharge	kg	6960	5822	7053	8142
Average Steam/CO2 during recharge	kg/kg	2.20	1.98	2.34	2.14
Average SRD during recharge	kJ/kg	4810	4331	5135	4682
CO2 captured in discharge	kg	4280	4131	3871	4707
CO2 released in recharge	kg	3168	2943	3008	3808
Pressurisation time	Hours: Mins	00:50	00:22	00:54	00:45

Due to the start-up and stabilization time of the stripper, in all cases the solvent could not be fully regenerated during the “recharging” phase. This means additional energy is required at a later time to fully strip the CO_2 from the stored solvent. Additionally this means the solvent was regenerated away from optimal operation point, greatly increasing the energy required to regenerate. Overall this meant the cycle efficiency was quite low in these tests. However these impacts could potentially be avoided and the process significantly improved.

In principle it should be possible to regenerate this solvent at the same or close to the same efficiency of normal optimum operation; for example a small steam flow to the stripper, could maintain the temperature and pressure, avoiding the majority of the stabilization time. Further these tests were penalized by the plant design; these were the following issues the design caused:

- The solvent tanks were integral part of the solvent loop, therefore when returning to operation all lean solvent had to be directly used in the absorber.

- Rich solvent could not be stored with the stripper operating due to solvent tank position meaning rich solvent must pass through the stripper. This also means on restart the stripper is full of rich solvent instead of lean solvent.

- As rich solvent must pass through stripper, the minimum steam flow to maintain pressure and temperature could not be tested as this would regenerate the solvent.

- Absorption could not be completed during regeneration, due to rich solvent passing through the absorber to reach the stripper.

Follow up work should ensure that an appropriate tank design is used to avoid the operational issues experienced here and allow these other process concepts to be demonstrated. Additionally one aspect on investigated in this analysis is that regeneration of stored solvent must occur at the same time as CO_2 is being captured. Therefore the capacity of stripper and how this is operated with power plant is crucial to optimize the regeneration and understand what conditions make this process economical.

In 2015 the OCTAVIUS project will complete a detailed economic analysis of several designs and operating modes for CCS plants (including solvent storage) in a flexible market model. It aims to identify the key drivers and potential methods to increase the flexibility of fossil plant with CCS technology while being competitive within electricity markets.

6. Conclusions

The solvent storage concept for improving the flexibility of fossil plants with CCS has been demonstrated at large scale at ENEL's pilot plant in Brindisi. Four tests were completed to assess different operating modes and conditions.

For all tests it was found it took significant amount of time for the stripper to stabilize and this meant in one pass the solvent could not be fully regenerated. This also resulted in the regeneration being at non-optimal conditions greatly increasing amount of energy requirement for regeneration. Overall these tests showed poor energy efficiency, however the process design of this pilot plant was not specifically planned for solvent storage. In particular the tanks were not located in ideal positions, meaning some compromises in the tests had to be taken. These compromises have had a significant impact on the results and reduced the possible tests that could be undertaken.

Follow up work should seek to ensure the plant design is appropriate for solvent storage to avoid the issues faced in this experiment.

The complete test of solvent storage requires economic assessment in flexible market model. This will be undertaken in OCTAVIUS in 2015, using some the data from this experiment as key inputs.

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